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(54) Titre : COMPOSES SYNERGIQUES DE POLYSACCHARIDES UTILISES COMME SUPERABSORBANTS OU  
ABSORBANTS NATURELS ET BIODEGRADABLES

(54) Title: SYNERGISTIC COMPOSITIONS OF POLYSACCHARIDES AS NATURAL AND BIODEGRADABLE  
ABSORBENT MATERIALS OR SUPERABSORBENTS

(57) Abrégé/Abstract:

The present invention relates to multi-component synergistic absorbent compositions comprising at least one polysaccharide and at least one or more polysaccharide-based components or gelling proteins. These compositions possess synergistic effects in their capacity to absorb water, saline solutions and biological fluids, at normal pressure or under load, or to retain these fluids, or a combination of these properties.



## **TITLE OF THE INVENTION**

SYNERGISTIC COMPOSITIONS OF POLYSACCHARIDES  
AS NATURAL AND BIODEGRADABLE ABSORBENT MATERIALS OR  
SUPERABSORBENTS

## 5 **FIELD OF THE INVENTION**

The present invention relates to synergistic compositions of polysaccharides as natural and biodegradable absorbent materials or superabsorbents. The compositions of the present invention show synergistic effects in their capacity to absorb water, saline solutions, biological fluids, and  
10 the like, at normal pressure or under load, and to retain these fluids.

## **BACKGROUND OF THE INVENTION**

Superabsorbent polymers are mainly used as absorbents for biological fluids, water, aqueous solutions and the like. These absorbents are primarily used in diapers, adult incontinence products as well as in  
15 feminine hygiene applications. Polyacrylates and polyacrylamides, as well as their copolymers, are among the best known superabsorbents. Alternative acrylic superabsorbent polymer forms, including partially biodegradable materials, are described in "*Modern Superabsorbent Polymer Technology*" (Buchholz F. L. and Graham A. T. Eds., Wiley-VCH, New York, 1998).

20 Commercial superabsorbents are mainly polyacrylate-based polymers. However, their biodegradability is questionable, especially for high molecular weight polymers. These polymers are synthesized from monomers such as acrylic acids and acrylamides. Following the polymerization process, there are still residual monomers or oligomers showing toxicity and allergenic  
25 potential.

These synthetic polymers have also been grafted onto polysaccharides. Superabsorbent polysaccharide-based grafted-polymers are obtained through the grafting of an unsaturated monomer (acrylonitrile, acrylic acid, acrylamide) onto starch or, less frequently, cellulose. The so-obtained polymers, also called "Super Slurper", illustrate a water absorption capacity ranging from 700 to 5300 g/g for deionised water, and up to 140 g/g in a 0.9 % saline solution (weight by volume of NaCl, referred hereinafter as saline solution) (Riccardo P.O., Water-Absorbent Polymers: A Patent Survey. J. Macromol.Sci., Rev. Macromol. Chem. Phys., 1994, 607-662 (p.634) and cited references). Despite their high water absorption capacity, these grafted polysaccharides, prepared by radical polymerization, are hypoallergenic and are not known to be biodegradable.

Among other polymers, polyaspartates have been recognized as offering good absorbent properties and as being biodegradable (Ross et al., US Patent 5,612,384). However, polyaspartates appear to have several drawbacks regarding their low molecular weight. Furthermore, polyaspartates are produced synthetically (Koskan et al., US Patent 5,221,733) from non-renewable sources such as for example maleic anhydride (obtained from butane). Finally, these polymers are strongly ionic and subject to performance fluctuations in saline solutions.

Polymeric blends and mixtures, used as absorbents or superabsorbents, are known. More specifically, the synergistic effect on the absorption against pressure of two synthetics polyacrylate-based hydrogel-forming particles has been reported (Schmid et al., EP 0 691 133 A1). Since these formulations comprise synthetic polymers, they are unsuitable in light of allergenic, abrasive, ecological or toxicological concerns.

Chmelir and Klimmek (US Patent 5,340,853), teach a synergistic absorbing and swelling agent consisting of at least two

components. The agent is made from a water-swellaable synthetic polymer or copolymer, crosslinked with a multifunctional compound, and a second component. The second component is a polysaccharide such as galactomannans or polygalactomannans. Alternatively, it could comprise  
5 admixtures of a galactomannan or polygalactomannans with other natural or synthetic polymers such as starch and modified starch. Even though the inventors refer to a synergistic effect when mixing the two components, no clear evidence for the synergy has been demonstrated when only polysaccharide components are used. Furthermore, since these formulations  
10 require synthetic polymers, such as polyacrylates, they are unsuitable for many uses in light of allergenic, abrasive, ecological or toxicological concerns.

Many other polyacrylate-polysaccharide based synergistic compositions have been disclosed such as those taught by Gunther, Klimmek, Brüggeman and Chmelir (US Patents 5,721,295; 5,847,031; 5,736,595;  
15 5,264,471; and 4,693,713 Reissue 33,839). However, since these formulations again require synthetic polymers, such as polyacrylates, they are unsuitable in light of allergenic, abrasive, ecological or toxicological concerns.

Renewable resources such as mixtures of polysaccharides have also been considered as absorbent materials. US Patent 5,801,116,  
20 granted to Rhodia Inc. (Cottrell et al.) discloses one or more polysaccharides having a particle size of greater than 200 mesh (74 microns), preferably modified guar gum. This modified guar gum may be used alone as an absorbent material or in combination with other known materials, such as natural or synthetic hydrophilic polymers. The inventors describe a potential  
25 synergistic absorbency when the compositions are combined with one or more of several classes of chemicals including simple carbohydrates (glucose, fructose, sorbitol, and the like) and synthetic hydrophilic polymers. However, no specific composition is exemplified to prove the synergistic hypothesis.

Furthermore, these guar absorbents have an undesirable tendency to give an syneresis effect (referred as slimy effect) to the wearer.

US Patent 4,454,055 (Richman et al.), issued to National Starch, teach synergistic interactions between ionically crosslinked polyelectrolytes (polyacrylates-starches), and modified starches or other  
 5 extenders. Because these ionically crosslinked polyelectrolytes are made mainly from synthetic SAPs (Super Absorbent Polymers), they are again unsuitable for many uses in light of allergenic, abrasive, ecological or toxicological concerns.

10 Polysaccharide-protein synergies have also been reported in the food industry. The synergistic compositions relate to the viscosity or texture enhancement of food gels (Alloncle M et al., Cereal Chemistry, 66 (2), 1989, pp. 90-93; Kaletung-Gencer G et al., Journal of Texture Studies, 17 (1), 1986, pp. 61-70; Alloncle M et al., Food Hydrocolloids, 5 (5), 1991, pp.455-  
 15 467; Sudhakar V et al., Food Chemistry, 55 (3), 1996, pp. 259-264; Rayment P et al., Carbohydrate polymers, 28 (2), 1995, pp. 121-130; Pellicer J et al., Food Science and Technology International, 6 (5), 2000, pp. 415-423; Tako M, Bioscience Biotechnology and Biochemistry, 56 (8), 1992, pp. 1188-1192; Tako M et al., Agricultural and Biological Chemistry, 52 (4), 1988, pp.1071-  
 20 1072; Murayama A et al., Bioscience, Biotechnology and Biochemistry, 59 (1), 1995, pp. 5-10; Goycoolea F.M et al., Gums and stabilizers for the food industry 7: proceedings of the 7th international conference in Wrexham, July, 1993, pp. 333-344). The reasons for being of these food gels is different when compared to those used in hygiene applications. Food gels aren't designed to  
 25 absorb or retain large amounts of saline or physiological fluids under pressure. Indeed, no synergistic effects have been reported in these publications concerning absorbent or superabsorbent technologies.

Glass-like, pregelatinized starches, have been disclosed by Groupe Lysac (Huppé et al. CA 2,308,537) as being a useful absorbent for liquids. However, these pregelatinized starches only absorb 8 g/g, which is too low to be useful in the hygiene industry. In order to improve the absorption capacity of these modified starches, they were mixed with xanthan and guar gums. The modified starches have also been blended in mixtures with sodium carboxymethyl cellulose (CMC). Some synergistic effects were observed but only in those cases where starches were admixed with specific concentrations of guar and xanthan gums. Moreover, the disclosed absorption capacities remained too low to be useful in the hygiene industry.

There thus remains a need for novel synergistic compositions of polysaccharides with improved performance as natural and biodegradable absorbent materials or superabsorbents.

The present invention seeks to meet these and other needs.

## 15 **SUMMARY OF THE INVENTION**

The present invention relates to synergistic compositions of polysaccharides as natural and biodegradable absorbent materials or superabsorbents. These synergistic compositions show an increased capacity to absorb liquids such as water, saline solutions and biological fluids, at normal pressure or under load, and to retain these fluids. Furthermore these synergistic compositions are based on natural sources, are biodegradable and non-toxic. More specifically, the present invention relates to synergistic absorbent or superabsorbent compositions comprising at least one polysaccharide and at least one polysaccharide-based component or gelling protein.

The present invention relates to synergistic compositions of polysaccharides to be used as natural, renewable and biodegradable absorbents or superabsorbents for personal hygiene products such as baby

diapers, incontinence products and sanitary napkins. The compositions can also be used in several other applications such as in food packaging absorbent pads; in agricultural and forestry applications to retain water in the soil and to release water to the roots of plants; in fire-fighting techniques; as  
5 bandages and surgical pads; for cleaning-up acidic or basic aqueous solution spills, including water soluble chemical spills; as polymeric gels for cosmetics and pharmaceuticals also known as drug delivery systems for the controlled release of active substances and; and finally for manufacturing artificial snow.

The present invention also relates to a multi-component  
10 synergistic absorbent composition comprising one or more modified starches and at least one or more components selected from a first component class selected from mannose containing polysaccharides, a second component class selected from ionic polysaccharides, and a third component class selected from gelling proteins or polypeptides.

15 The present invention further relates to a multi-component synergistic absorbent composition comprising one or more ionic polysaccharides and at least one or more components selected from a first component class selected from mannose containing polysaccharides and a second component class selected from gelling proteins or polypeptides.

20 Further scope and applicability will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of example only, since various changes and modifications will become apparent to those skilled in the art.

## 25 **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows a comparison between measured FSC values and calculated additive values in 0.9% NaCl solution for different ratios

of guar gum and starch. A weak synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values.

5                   Figure 2 shows a comparison between measured CRC values and calculated additive values in 0.9% NaCl solution for different ratios of guar gum and starch. A weak synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values.

10                  Figure 3 shows a comparison between measured FSC values and calculated additive values in 0.9% NaCl solution for different ratios of CMC and starch. No synergistic effect is observed.

15                  Figure 4 shows a comparison between measured CRC values and calculated additive values in 0.9% NaCl solution for different ratios of CMC and starch. A strong synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values.

20                  Figure 5 shows a comparison between measured FSC values and calculated additive values in 0.9% NaCl solution for different ratios of CMC and guar gum. A weak synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values.

25                  Figure 6 shows a comparison between measured CRC values and calculated additive values in 0.9% NaCl solution for different ratios of CMC and guar gum. A strong synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values.

Figure 7 shows a comparison between measured FSC values and calculated additive values in 0.9% NaCl solution for different ratios



of starch, CMC and guar gum. A synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values.

Figure 8 shows a comparison between measured CRC values and calculated additive values in 0.9% NaCl solution for different ratios of starch, CMC and guar gum. A synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values. The figure also shows a synergistic effect in the absence of starch.

Figure 9 shows a comparison between measured AUL values and calculated additive values in 0.9% NaCl solution for different ratios of starch, CMC and guar gum. A synergistic effect is observed when higher values are obtained as compared to the corresponding calculated additive values.

Figure 10 shows a comparison between measured viscosity values and calculated additive values in 0.9% NaCl solution for different ratios of starch, CMC and guar gum. No synergistic effects are observed.

### **DETAILED DESCRIPTION OF THE INVENTION**

The present description refers to a number of routinely used chemical terms. Nevertheless, definitions of selected terms are provided for clarity and consistency.

As used herein the term polysaccharide refers to a combination of nine or more monosaccharides, linked together by glycosidic bonds, and include starch, modified starch, cellulose, etc.

As used herein, the term "modified" starch means a starch that is pregelatinized, thermally inhibited [Jeffcoat et al. (US Patents 5,720,822; 6,261,376; 6,016,574), Chung-Wai et al. (US Patents 5,932,017;

6,231,675; 6,451,121), Shah et al. (US Patent 5,718,770), Shi et al. (US Patent 6,277,186)], extruded, jet-cooked, dextrinated, hydrolyzed, oxidized, covalently cross-linked, alkylated, hydroxyalkylated, carboxyalkylated, esterified, fractionated in its amylose or amylopectin constituents.

5                   As used herein, the term "Free Swell Capacity" (FSC), also called Absorption, refers to the amount (g) of fluid absorbed (0.9% Weight/volume NaCl solution, thereafter called 0,9 % NaCl solution) per gram of the composition.

                  As used herein, the term "Centrifuge Retention Capacity"  
10 (CRC) also called Retention, refers to the amount (g) of fluid absorbed (0.9% NaCl solution) per gram of the composition.

                  As used herein, the term "Absorption Under Load" (AUL) at 0.3 PSI (2.06 KPa), also called Absorption Against Pressure, refers to the amount (g) of substance absorbed (0.9% NaCl solution) per gram of the  
15 composition, using 0.1 g of absorbent in the apparatus.

                  As used herein, the term "ionic polysaccharides" refers to both anionic or cationic polysaccharides.

                  In a broad sense, the present invention relates to synergistic compositions of polysaccharides as natural and biodegradable absorbent  
20 materials or superabsorbents. It was discovered that the absorbing characteristics of modified starches can be synergistically improved by the addition of a polysaccharide composed of mannose, an ionic polysaccharide, gelling proteins or a combination thereof. Furthermore, it was discovered that the performances of ionic polysaccharides can be improved by the addition of  
25 mannose containing polysaccharides, gelling proteins or a combination thereof.

                  Examples of anionic polysaccharides are selected from the

group consisting of sodium, lithium, potassium, and ammonium salts of carboxyalkylated cellulose (like carboxymethyl cellulose), as well as oxidized cellulose, pectin, arabic gum, kappa, iota or lambda carrageenans, agar-agar or alginates. Examples of cationic polysaccharides are selected from the group  
 5 consisting of chloride, bromide, iodide, nitrate, phosphates, sulfates and organic salts of chitosan, as well as cationic cellulose.

These polysaccharide compositions, in order to be suitable for absorption purposes, should have a mean particles size ranging from about 80  $\mu\text{m}$  to about 800  $\mu\text{m}$  and more preferably from about 150  $\mu\text{m}$  to about 600  
 10  $\mu\text{m}$ . In order to avoid particle migration, the particles should be homogeneously blended. In order to achieve a homogeneous blending, the size of the particles should not vary by more than about 200  $\mu\text{m}$ . A process for producing the compositions is provided.

The absorbent or superabsorbent synergistic  
 15 polysaccharides compositions, in accordance with the present invention, are prepared with different ratios of individual components, as illustrated in Examples 1 to 57. These compositions are then characterized by their Free Swell Capacity (FSC), their Centrifuge Retention Capacity (CRC) as well as their Absorption Under Load (AUL) capacity at 0.3 PSI (2.06 KPa). The FSC  
 20 and CRC are standard methods in the field of superabsorbents, used for all applications in personal hygiene. AUL is a standard test for baby diapers.

A synergistic effect for a multi-component system is observed when the measured value of the AUL, FSC and CRC is higher than the calculated additive value.

25 Typical compositions of polysaccharides, as disclosed in the present invention, are represented by the following equation:

$$A_a + B_b + N_n = 1$$

wherein, A is the composition fraction (weight by weight or referred to hereinafter as W/W) of modified starch or ionic polysaccharides, when these polysaccharides are used as the primary constituent; B represents the composition fraction (W/W) of a mannose containing polysaccharide, a gelling protein or an ionic polysaccharide (when starch is the primary constituent of the composition); N represents the composition fraction (W/W) of supplemental constituents, these constituents being composed of one or more polysaccharides or proteins, selected from mannose containing polysaccharides, gelling proteins, ionic polysaccharides or modified starches (when applicable). It is important to note that N is a optional number and it is contemplated that as many Ns as required can be used in order to improve the synergistic effects.

A specific CRC, AUL and FSC can be attributed to each component. In other words, the first component of the synergistic blend has an AUL, FSC, and CRC value corresponding to  $AUL_a$ ,  $FSC_a$  and  $CRC_a$ , and has a composition fraction (W/W) A. The second component has a composition fraction (W/W) B, and has  $AUL_b$ ,  $FSC_b$  and  $CRC_b$  values. Other optional components have a composition fraction (W/W) N, and  $AUL_n$ ,  $FSC_n$  and  $CRC_n$  values.

The Absorption Under Load (AUL), the Free Swell Capacity (FSC), and the Centrifuge Retention Capacity (CRC) of the blends, [ $AUL_{a+b+n}$ ,  $FSC_{a+b+n}$  and  $CRC_{a+b+n}$ ] can be calculated and expressed as follows:

$$\begin{aligned} AUL_{a+b+n} &= A \bullet AUL_a + B \bullet AUL_b + N \bullet AUL_n \\ FSC_{a+b+n} &= A \bullet FSC_a + B \bullet FSC_b + N \bullet FSC_n \\ CRC_{a+b+n} &= A \bullet CRC_a + B \bullet CRC_b + N \bullet CRC_n \end{aligned}$$

A synergistic effect is observed when the measured AUL, FSC and CRC results of the composition are higher than the calculated additive ones, [ $AUL_{a+b+n}$ ,  $FSC_{a+b+n}$  and  $CRC_{a+b+n}$ ].

Synergistic effects were observed in many complex polysaccharide compositions comprising at least one polysaccharide and at least one or more polysaccharide-based components or gelling proteins. These synergistic effects occur more often, and are more important, when  
5 three or more compounds selected from these classes are present in the composition. These synergistic effects are also more important when the primary constituent of the composition is selected from the class of modified starches or ionic polymers. Significant synergistic effects are also observed when more than one product of a same class is used.

10 The first component class of the compositions of the present invention can be selected from the modified starches. These modified starches can be obtained from diversified sources, such as corn, waxy corn, wheat, waxy wheat, rice, waxy rice, potato, tapioca, waxy maize, sorghum, waxy sorghum, sago, barley, and amaranth. In order to be useful for the  
15 applications as contemplated by the present invention, these modified starches can be dextrinated, hydrolyzed, oxidized, covalently crosslinked, alkylated, hydroxyalkylated, carboxyalkylated, carboxymethylated, acetylated or esterified, fractionated (e.g. amylose and amylopectin), and physically modified by thermal inhibition, jet-cooking or extrusion.

20 Oligomeric polyethylene glycol crosslinked polysaccharides have been previously described by Groupe Lysac (Couture et al., CA 2,362,006) as being particularly useful as modified starches. Other examples of physically modified starches have been described by Groupe Lysac (Huppé et al., CA 2,308,537). In the latter, a pregelatinized, glass-like starch was  
25 disclosed, which was subsequently found to be useful as a modified starch for the compositions of the present invention.

Other modified starches, such as those disclosed by Kimberly-Clark (Qin et al., US Patents 5,550,189; 5,498,705, and 5,470,964),

SCA (Besemer et al., WO 00/35504A1, WO 01/34656A1 and WO 99/29352A1), Beenackers A. A. C. M. et al. (Carbohydr. Polym., 2001, 45, 219-226) and National Starch (Jeffcoat et al. US Patents 5,720,822; 6,261,376; 6,016,574; Chung-Wai et al. US Patents 5,932,017; 6,231,675; US 5 6,451,121; Shah et al. US Patent 5,718,770; Shi et al. US Patent 6,277,186), could also be used in the compositions of the present invention. These modified starches constitute only a few examples of modified starches useful for the absorbent compositions of the present invention. Because these modified starches already have some absorbent properties, and exhibit less 10 syneresis (slimy effect) than other polysaccharides, they are preferred as the primary constituent of the compositions of the present invention.

The second component class of the compositions of the present invention can be selected from the mannose containing polysaccharides. These polysaccharides comprise glucomannans or 15 polyglucomannans such as konjac gum, or konjac flour. This class also comprises galactomannans or polygalactomannans, such as Guar gum, Locust bean gum, Mesquite gum, Tara gum, Phyllium extracts and Fenugreek extracts, in addition to comprising Aloe mannans.

The mannose containing polysaccharides can be used in 20 their natural, unmodified form as well as in a physically or chemically modified form. The mannose containing polysaccharides can be hydrolyzed, oxidized, covalently crosslinked, alkylated, hydroxyalkylated, carboxyalkylated, carboxymethylated, acetylated or esterified, and physically modified by extrusion, jet-cooking or other processes.

25 The third component class of the compositions of the present invention is an ionic polysaccharide-based compound. Ionic polysaccharides can be both anionic and cationic. Examples of suitable cationic polysaccharides are selected from the group consisting of chlorides,

bromides, iodides, nitrates, sulfates, phosphates and organic salts of cationic polysaccharides, as well as cationic cellulose or chitosan salts.

Anionic polysaccharides are the preferred third component class for the compositions of the present invention. They can be in their sodium, lithium, potassium or ammonium salt forms. Sodium carboxymethyl cellulose (CMC) is the preferred ionic component. Other useful ionic polysaccharides are sodium alginate and alginate compositions, xanthan gum, kappa, iota and lambda carageenan gums, karaya gum, arabic gum, pectin, agar-agar, oxidized cellulose and sulfated cellulose.

The ionic polysaccharides can be used in their natural, unmodified form, as well as in a physically or chemically modified form. The ionic polysaccharides can be hydrolyzed, oxidized, covalently crosslinked, alkylated, hydroxyalkylated, carboxyalkylated, carboxymethylated, acetylated or esterified, and physically modified by extrusion, jet-cooking or other processes.

Since the ionic polysaccharides exhibit high absorption properties, they are also the preferred primary constituent for the compositions of the present invention.

The fourth component class of the compositions of the present invention are gelling proteins or polypeptides. Because these compounds are biodegradable and based on renewable sources, they provide a wide array of synergistic effects suitable to the compositions of the present invention. Examples of suitable gelling proteins or polypeptides are gelatin, collagen, albumin, ovalbumin, bovine albumin, casein, keratin, keratose, Whey proteins, Whey proteins isolates, soybean proteins, soy proteins, soy proteins isolate, polyaspartic acid or its salts, zein and gluten. Preferred gelling proteins are gelatin, as well as casein and its salts.

The gelling proteins can be used in their natural, unmodified form, as well as in a physically or chemically modified form. The gelling proteins can be hydrolyzed, oxidized, covalently crosslinked, alkylated, hydroxyalkylated, carboxyalkylated, carboxymethylated, acetylated or esterified, and physically modified by extrusion, jet-cooking or other processes.

In order to provide the desired synergistic effects, the selected compounds must be homogeneously mixed. Mixing techniques are widely known in the art and are described in Perry's Chemical Engineers' Handbook (7<sup>th</sup> edition, McGraw-Hill, 1997, ISBN: 0070498415).

Typical compositions can be mixed using double cone mixers, twin shell mixers, horizontal drum (with or without baffles), double cone revolving around long axis (with or without baffles), ribbon mixers, vertical screw mixers, batch Muller mixers, continuous Muller mixers, twin rotor mixers, single rotor or turbine mixers. Other mixing techniques applicable to the compositions of the present invention will become apparent to a skilled technician in the art, and are contemplated as being within the scope of the present invention.

The polysaccharides and gelling proteins should have a specific particle size in order for the compositions to be suitable for absorption purposes. The mean particulate size of these components should not be below 80  $\mu\text{m}$ , in order to avoid fine particulate problems (Occupational Safety and Health problems). In order to facilitate water, saline or physiological fluid penetration inside the particulates (to avoid a phenomenon called gel blocking), the particulates should not have a mean particulate size greater than 800  $\mu\text{m}$ . Particularly efficient synergistic compositions were obtained with mean particulate sizes ranging from about 150  $\mu\text{m}$  to about 600  $\mu\text{m}$ .

In order to obtain homogenous compositions the additional components (like B or N components) should have a similar mean particulate



size. Particulate migration can be avoided if the size of the additional components of the compositions does not vary by more than 200  $\mu\text{m}$  from the primary component (modified starches or, when no modified starches are used, ionic polysaccharides).

5                   The absorbent materials or superabsorbents described in the present invention, may be incorporated into absorbent personal hygiene products such as, for example, baby diapers, incontinence products, sanitary napkins and the like. They could be also used in absorbent members, like absorbent cores, airlaids or foamed structures. These absorbent members are  
10                   mainly made from superabsorbents, cellulosic fibers or man-made fibers and bi-component thermoplastic fibers (known also as BICO).

                  Furthermore, the absorbent compositions could also be used in several other applications, such as in food pads; in agricultural and forestry applications to retain water in the soil and to release water to the roots  
15                   of plants; in fire-fighting techniques; as bandages and surgical pads; for cleanup of acidic or basic aqueous spills, including water soluble chemical spills; as polymeric gels for cosmetics and pharmaceuticals (also known as drug delivery systems) for the controlled release of active substances; and for artificial snow.

20                   As was previously mentioned, a synergistic effect for a multi-component polysaccharide system is observed when the measured value of the AUL, FSC and CRC is higher than the calculated additive value. This can be observed when at least two or more compound classes are used together. More specifically, synergistic effects were observed in many complex  
25                   polysaccharide compositions comprising at least one polysaccharide and at least one or more polysaccharide-based components or gelling proteins.

                  A slight but significant synergistic effect can be observed on the FSC and CRC for two component blends including Guar gum and Starch

(Table I, Figures 1 and 2). No synergistic effect on the FSC is observed for blends containing CMC and Starch. However these blends exhibit a strong synergistic effect on the CRC (Table I, Figures 3 and 4). A slight but significant synergistic effect on the FSC, is also observed for blends containing CMC and  
5 Guar gum (Table I, Figure 5). However, these blends exhibit a strong synergistic effect on the CRC (Table I, Figure 6).

As demonstrated, an AUL, FSC or CRC can be observed in two-component compositions, but rarely simultaneously for each measurement. In order to observe a synergistic effect on all the  
10 measurements, three or more component blends must be used. These multi-component blends preferably contain a component from each of the three classes described hereinabove.

Polysaccharide three-component blends containing 0-70 % Starch, 9-30 % CMC, and 21-70% Guar Gum, and preferably between 10-60%  
15 Starch, 12-27 % CMC, and 28-63% Guar Gum demonstrate a strong synergistic effect by increasing values of FSC up to 44 g/g with a synergistic effect near 5 g/g (Table II, Figure 7).

Similarly, polysaccharide three-component blends or mixtures containing 0-70 % Starch, 9-30 % CMC, and 21-70% Guar Gum, and  
20 preferably between 10-60% Starch, 12-27 % CMC, and 28-63% Guar Gum demonstrate a synergistic effect by increasing values of CRC up to 34 g/g with a synergistic effect near 9 g/g (Table II, Figure 8).

Similarly, polysaccharide three-component blends or mixtures containing 0-70 % Starch, 9-30 % CMC, and 21-70% Guar Gum, and  
25 preferably between 10-60% Starch, 12-27 % CMC, and 28-63% Guar Gum demonstrate a synergistic effect by increasing values of AUL up to 25 g/g with a synergistic effect near 5 g/g (Table II, Figure 9).

A synergistic effect on the viscosity was not observed (Table II, Figure 10).

Examples 51 to 57 illustrate the use of gelling proteins and polypeptides such as gelatin and calcium caseinates, added to the complex synergistic polysaccharides formulations.

The use of other natural polysaccharides or gelling proteins in the composition of the present invention leads to significant synergistic effects as illustrated in Examples 29 to 50 (Tables III to VII). These results illustrate synergistic compositions with performances comparable to those obtained with synthetic superabsorbent polymers such as polyacrylates and polyacrylamides.

The present invention is illustrated in further detail by the following non-limiting examples.

#### Starting Materials

Pre-gelatinized wheat starch A (ADM-Ogilvie), sodium carboxymethyl cellulose (CMC aqualon; Hercules) and crude unmodified guar gum (L.V. Lomas Ltd.) have been used as starting materials for examples 1 to 28.

Modified starches such as carboxymethylstarch and esterified starches crosslinked with triglycoldichloride were provided by Lysac Technologies Inc.

Crude unmodified guar gum (Starlight), crude unmodified konjac gum (LIMAO Agricultural products), CMC aqualon (Hercules), xanthan gum (ADM), sodium alginate (Tic Gums), carrageenan (CP Kelco), pectin LM (Tic Gum) and chitosan Chito Clear (Primex) have been used as starting materials for examples 29 to 57.

### AUL measurements

The Absorption Under load (AUL) in a 0.9% NaCl solution at 0.3 psi was determined according to the recommended test method 442.1-99 from EDANA<sup>2</sup>, using 0.1 gram of the absorbent in the apparatus.

### 5 FSC and CRC measurements (using tea bags)

Tea bags (10 X 10 cm) were made from heat sealable Ahlstrom filter paper  $16.5 \pm 0.5$  g/m<sup>2</sup>.

### FSC measurements

10 The Free Swell Capacity (FSC) in a 0.9% NaCl solution was determined according to the recommended test method 440.1-99 from EDANA.<sup>3</sup>

### CRC measurements

15 The Centrifuge Retention Capacity (CRC) in a 0.9% NaCl solution was determined according to the recommended test method 441.1-99 from EDANA.<sup>4</sup>

### Viscosity measurements

The viscosity was measured with a Brookfield RV DV II+ viscometer at 50 RPM with a spindle No 6, using a 2% (W/W) solution made with a 0.9% NaCl solution and agitated for one hour before measurement.

### 20 Gel strength measurements

The gel strength was measured using a TA.XT2i from Texture Technologies with a cylindrical probe TA-12, load capacity 5Kg, gain trigger 0.5 g, displacement 10 mm, time 5 seconds, speed 2.0 mm /second. The gel strength is expressed in force (g).

### 25 Biodegradability and ecological impact

According to the United States Environmental Protection Agency (EPA), the Zahn-Wellens test is useful for testing the biodegradability

of a substance soluble in water to at least 50 mg of dissolved organic carbon (DOC) per liter (US Environmental Protection Agency (EPA), Fate, Transport and Transformation Test Guidelines, OPPTS 832.3200, Zahn-Wellens / EMPA test, EPA712-C-98-084, January 1998).<sup>5</sup> For substances that are not completely soluble, it offers only a qualitative indication of whether these substances are basically susceptible to biological degradation or not (Buchholz et al., US Patent 5,789,570). An activated sludge was used in Example 27 to evaluate the biodegradability. A technicon carbon analyzer was used to measure the DOC and the percentage biodegradability was calculated according to the DOC obtained, and reported in the equation given in reference 4. Example 27 showed no toxicity for microorganisms and no toxic product was detected that would destroy the aquatic fauna, particularly the micro crustacean *Daphnia magna*. Mineral medium was used as a blank and the positive control was ethylene glycol, which showed 100% biodegradability after 14 days.

#### Composition percentages

Composition percentages are all related in weight by weight (w/w) percentages.

#### Hypoallergenicity

Hypoallergenicity tests were performed by the Consumer Product Testing Co. according to the ASTM D6355-8 norm<sup>6</sup>; performed with adherence to ICH Guideline E6 for good clinical practice and requirements provided for in 21 CFR parts 50 and 56 in accordance to standard operating procedures and applicable protocols. The products have been tested with sixty (60) qualified subjects, male and female, ranging in age from 20 to 72 years.

The upper back, between the scapulae, served as the treatment area. Approximately 0.2 g of the material was applied to the  $\frac{3}{4}$ " x  $\frac{3}{4}$ " absorbent pad portion of a saline moistened adhesive dressing. Patches were

- applied three times per week (e.g. Monday, Wednesday and Friday) for a total of nine (9) applications. The site was marked to ensure the continuity of patch application. Following supervised removal and scoring of the first induction patch, participants were instructed to remove all subsequent induction patches at home, twenty-four hours after application.

The following evaluation key was used by all participants:

- 0 : No visible skin reaction;
- + : Barely perceptible or spotty erytherma;
- 1 : Mild erytherma covering most of the test site;
- 2 : Moderate erytherma, possible presence of mild edema;
- 3 : Marked erytherma, possible edema;
- 4 : Severe erytherma, possible edema, vesiculation, bullae or ulceration.

### **EXAMPLES 1 to 15**

#### **Synergy for FSC and CRC with two component blends**

- Two component blends (examples 1 to 15) comprising Guar Gum and Starch, CMC and Starch, CMC and Guar Gum were prepared by weighing 0, 25, 50, 75 and 100 % of each material. The blends were mixed vigorously in a 20 ml vial. The Free Swell Capacity (FSC) and Centrifuge Retention Capacity (CRC) was measured for each of the two component blends, and was subsequently compared with calculated additive values based on component performances. The results are illustrated in Table I, as well as in Figures 1 to 6.

TABLE I: Examples for two-component blends									
Example	Blends			Measured		Calculated		Synergy	
	Guar Gum	CMC B315	Starch	FSC	CRC	FSC	CRC	FSC	CRC
	%	%	%	g/g	g/g	g/g	g/g	g/g	g/g
1	100	0		32.48	22.72	32.48	22.72	0.00	0.00
2	75	25		44.50	33.17	41.49	24.64	3.02	8.54
3	50	50		52.10	38.61	50.49	26.55	1.61	12.06
4	25	75		61.20	45.89	59.50	28.47	1.71	17.43
5	0	100		68.50	30.38	68.50	30.38	0.00	0.00
6	0		100	6.20	4.04	6.20	4.04	0.00	0.00
7	25		75	14.00	10.46	12.77	8.71	1.23	1.75
8	50		50	20.65	13.48	19.34	13.38	1.31	0.10
9	75		25	26.10	18.03	25.91	18.05	0.19	-0.02
10	100		0	32.48	22.72	32.48	22.72	0.00	0.00
11		0	100	6.20	4.04	6.20	4.04	0.00	0.00
12		25	75	20.41	15.01	21.78	10.63	-1.37	4.39
13		50	50	34.55	25.84	37.35	17.21	-2.80	8.63
14		75	25	52.44	36.64	52.93	23.80	-0.48	12.85
15		100	0	68.50	30.38	68.50	30.38	0.00	0.00
Components performances									
				Measured					
				FSC			CRC		
				g/g			g/g		
Starch 2604				6.20			4.04		
Guar Gum				32.48			22.72		
CMC Aqualon B315				68.50			30.38		

### EXAMPLES 16 to 26

#### Synergy for FSC, CRC, AUL and viscosity with three component blends

- 5 Three component blends (examples 16 to 26) were prepared by weighing 0 to 100 % of Starch, 0 to 30 % of CMC and 0 to 70 % of Guar Gum. The blends were mixed vigorously in a 20 ml vial. The FSC, CRC, Absorption under load (AUL) and viscosity was measured for each of the three component blends, and was subsequently compared with calculated
- 10 additive values based on component performances. The results are illustrated in Table II, as well as in Figures 7 to 10.

TABLE II : Examples for a three-component blend

TABLE II : Examples for a three-component blend											
Example	Blends			Measured				Calculated			
	Guar Gum	CMC B315	Starch	FSC	CRC	AUL	Visc.	FSC	CRC	AUL	Visc.
	%	%	%	g/g	g/g	g/g	cP	g/g	g/g	g/g	cP
16	0	0	100	6.20	4.04	17.09	80	6.20	4.04	17.09	80
17	7	3	90	9.57	7.55	17.98	100	9.91	6.14	17.78	569
18	14	6	80	13.62	10.83	18.07	160	13.62	8.24	18.46	1059
19	21	9	70	18.94	13.50	18.54	280	17.33	10.33	19.15	1548
20	28	12	60	22.70	16.67	18.28	760	21.03	12.43	19.84	2038
21	35	15	50	27.12	20.83	21.23	1380	24.74	14.53	20.53	2527
22	42	18	40	31.72	23.72	25.57	2160	28.45	16.63	21.21	3016
23	49	21	30	37.08	25.73	24.05	3160	32.16	18.72	21.90	3506
24	56	24	20	40.51	27.02	23.83	2580	35.87	20.82	22.59	3995
25	63	27	10	43.56	30.17	23.79	3360	39.58	22.92	23.28	4485
26	70	30	0	43.38	33.88	25.50	6100	43.29	25.02	23.96	4974
				Synergy							
				FSC	CRC	AUL	Visc.				
				g/g	g/g	g/g	cP				
16				0.00	0.00	0.00	0				
17				-0.34	1.41	0.20	-469				
18				0.00	2.59	-0.39	-899				
19				1.61	3.17	-0.61	-1268				
20				1.67	4.24	-1.56	-1278				
21				2.38	6.30	0.70	-1147				
22				3.27	7.09	4.36	-856				
23				4.92	7.01	2.15	-346				
24				4.64	6.20	1.24	-1415				
25				3.98	7.25	0.51	-1125				
26				0.09	8.86	1.54	1126				
Component performances											
				Measured							
				FSC	CRC	AUL	Visc.				
				g/g	g/g	g/g	cP				
	Starch 2604			6.20	4.04	17.09	80				
	Guar Gum			32.48	22.72	20.96	420				
	CMC Aqualon B315			68.50	30.38	30.97	15600				



**EXAMPLE 27****Biodegradability, hypoallergenisity, FSC, CRC and AUL of three component blend**

Pregelatinized Wheat Starch (15 Kg, 50 %, 30-170 mesh  
 5 (147 to 589 microns)); CMC (3.9 Kg, 13 %, 30-170 mesh (147 to 589 microns)); and guar gum (11.1 Kg, 37 %, 30-170 mesh (147 to 589 microns)) were vigorously mixed in a double action mixer (LELAND 100 DA-70, 40 Kg capacity) over a period of 15 minutes.

FSC = 29.0 g/g

10 CRC = 20.3 g/g

AUL = 20.0 g/g

Biodegradability: 91.1 % after 28 days.

Hypoallergenicity : Panel No. 20020142, No visible skin reaction (0) for all sixty (60) qualified subjects, on all nine (9) applications.

15

**EXAMPLE 28****Effects on the FSC, CRC, AUL, gel strength and viscosity of ionic polysaccharides having different viscosities**

Pregelatinized Wheat Starch (1000 Kg, 44.67 % (ADM));  
 Guar Gum Procol (900 Kg, 40.21 % (LV Lomas)); CMC Aqualon (114 Kg, 5.07  
 20 % (Hercules)); CMC Gabrosa (125 Kg, 5.58 % (Akzo Nobel)); and CMC (100 Kg, 4.47 % (Amtex)) were mixed in an industrial mixer for 10 minutes.

FSC = 27.47 g/g

CRC = 23.53 g/g

AUL = 21.69 g/g

25 Gel strength = 25.01 g

Viscosity = 2180 Centipoises (Cp)

**EXAMPLES 29 to 32****Effect on the FSC, CRC and AUL of three-component blends, of  
different starch based products.**

Four different starch based products (44.67 %) were mixed  
 5 with Guar Gum (40.21 %) and CMC (15.12 %) as described in Examples 1 to  
 15. The different starch based products used were pregelatinized wheat starch  
 (ADM), sodium carboxymethyl wheat starch crosslinked with triglycol dichloride  
 (Lysac Technologies Inc.), sodium maleate wheat starch crosslinked with  
 triglycol dichloride (Lysac Technologies Inc.), and a hybrid of the latter two  
 10 (Lysac Technologies Inc.). The results are illustrated in Table III.

TABLE III: Examples for a three-component blend with different starch based product, guar gum and CMC										
Example	Blends			Starch type	Measured			Calculated		
	Guar Gum	CMC B315	Starch		FSC	CRC	AUL	FSC	CRC	AUL
	%	%	%		g/g	g/g	g/g	g/g	g/g	g/g
29	40.21	15.12	44.67	1	35.71	33.13	27.2	30.26	26.06	18.36
30	40.21	15.12	44.67	2	47.88	43.51	30.50	39.96	32.45	26.95
31	40.21	15.12	44.67	3	38.33	35.38	26.26	36.39	28.43	26.10
32	40.21	15.12	44.67	4	38.31	34.64	32.04	36.39	29.32	23.57
					Synergy					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
29				1	5.35	7.07	8.84			
30				2	7.92	11.06	3.55			
31				3	1.94	6.95	0.16			
32				4	1.92	5.32	8.47			
Component performances										
					Measured					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
Starch type 1: Pregel 2604 (ADM)					6.50	4.70	11.47			
Starch type 2: Carboxymethyl crosslinked with TEG					28.00	19.00	30.70			
Starch type 3: Maleate crosslinked with TEG					20.00	10.00	28.81			
Starch type 4: Hybrid crosslinked with TEG					20.00	12.00	23.14			
Guar Gum (Starlight)					48.73	45.68	22.60			
CMC Aqualon B315					52.00	37.00	27.41			

**EXAMPLES 33 to 36****Effect on the FSC, CRC and AUL of three-component blends, of  
different starch based products**

Four different starch based products (44.67 %) were mixed  
 5 with Konjac Gum (40.21 %) and CMC (15.12 %) as described in Examples 1  
 to 15. The different starch based products used were pregelatinized wheat  
 starch (ADM), sodium carboxymethyl wheat starch crosslinked with triglycol  
 dichloride (Lysac Technologies Inc.), sodium maleate wheat starch crosslinked  
 with triglycol dichloride (Lysac Technologies Inc.) and a hybrid of the latter two  
 10 (Lysac Technologies Inc.). The results are illustrated in Table VI.

TABLE IV: Examples for a three-component blend with different starch based product, konjac gum and CMC										
Example	Blends			Starch type	Measured			Calculated		
	Konjac	CMC B315	Starch		FSC	CRC	AUL	FSC	CRC	AUL
	%	%	%		g/g	g/g	g/g	g/g	g/g	g/g
33	40.21	15.12	44.67	1	32.99	29.55	21.84	29.56	25.34	17.16
34	40.21	15.12	44.67	2	39.75	36.92	22.21	39.16	31.73	25.75
35	40.21	15.12	44.67	3	33.98	31.33	32.20	35.59	27.71	24.90
36	40.21	15.12	44.67	4	34.32	31.07	27.14	35.59	28.60	22.37
					Synergy					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
33				1	3.43	4.21	4.68			
34				2	0.59	5.19	-3.54			
35				3	-1.61	3.62	7.30			
36				4	-1.27	2.47	4.77			
Component performances										
					Measured					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
Starch type 1: Pregel 2604 (ADM)					6.50	4.70	11.47			
Starch type 2: Carboxymethyl crosslinked with TEG					28.00	19.00	30.70			
Starch type 3: Maleate crosslinked with TEG					20.00	10.00	28.81			
Starch type 4: Hybrid crosslinked with TEG					20.00	12.00	23.14			
Konjac Gum (LIMAO)					46.73	43.89	19.62			
CMC Aqualon B315					52.00	37.00	27.41			

**EXAMPLES 37 to 40****Effect on the FSC, CRC and AUL of three-component blends, of  
different starch based products**

Four different starch based products (44.67 %) were mixed  
 5 with Guar Gum (40.21 %) and sodium Alginate (15.12 %) as described in  
 Examples 1 to 15. The different starch based products used were  
 pregelatinized wheat starch (ADM), sodium carboxymethyl wheat starch  
 crosslinked with triglycol dichloride (Lysac Technologies Inc.), sodium maleate  
 wheat starch crosslinked with triglycol dichloride (Lysac Technologies Inc.) and  
 10 a hybrid of the latter two (Lysac Technologies Inc.). The results are illustrated  
 in Table V.

TABLE V: Examples for a three-component blend with different starch based product, guar gum and sodium alginate										
Example	Blends			Starch type	Measured			Calculated		
	Guar %	Alginate %	Starch %		FSC g/g	CRC g/g	AUL g/g	FSC g/g	CRC g/g	AUL g/g
37	40.21	15.12	44.67	1	35.88	33.12	21.42	29.70	24.15	18.25
38	40.21	15.12	44.67	2	46.95	40.06	26.23	39.30	30.54	26.84
39	40.21	15.12	44.67	3	39.40	33.51	28.69	35.73	26.52	26.00
40	40.21	15.12	44.67	4	36.85	31.60	31.80	35.73	27.41	23.47
					Synergy					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
37				1	6.18	8.97	3.17			
38				2	7.65	9.52	-0.61			
39				3	3.67	6.99	2.69			
40				4	1.12	4.19	8.33			
Component performances										
					Measured					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
Starch type 1: Pregel 2604 (ADM)					6.50	4.70	11.47			
Starch type 2: Carboxymethyl crosslinked with TEG					28.00	19.00	30.70			
Starch type 3: Maleate crosslinked with TEG					20.00	10.00	28.81			
Starch type 4: Hybrid crosslinked with TEG					20.00	12.00	23.14			
Sodium alginate (Tic Gums)					45.02	33.88	26.14			
Guar gum (Starlight)					48.73	45.68	22.60			

**EXAMPLES 41 to 44****Effect on the FSC, CRC and AUL of three-component blends, of  
different starch based products**

Four different starch based products (44.67 %) were mixed  
 5 with Guar Gum (40.21 %) and Konjac Gum (15.12 %) as described in  
 Examples 1 to 15. The different starch based product used were  
 pregelatinized wheat starch (ADM), sodium carboxymethyl wheat starch  
 crosslinked with triglycol dichloride (Lysac Technologies Inc.), sodium maleate  
 wheat starch crosslinked with triglycol dichloride (Lysac Technologies Inc.) and  
 10 a hybrid of the latter two (Lysac Technologies Inc.). The results are illustrated  
 in Table VI.

TABLE VI: Examples for a three-component blend with different starch based product, guar and konjac gum										
Example	Blends			Starch type	Measured			Calculated		
	Starch %	Guar %	Konjac %		FSC g/g	CRC g/g	AUL g/g	FSC g/g	CRC g/g	AUL g/g
41	40.21	15.12	44.67	1	32.49	30.42	27.26	29.56	27.10	17.18
42	40.21	15.12	44.67	2	43.27	40.25	27.20	39.17	33.49	25.77
43	40.21	15.12	44.67	3	36.55	34.06	31.96	35.59	29.47	24.92
44	40.21	15.12	44.67	4	37.02	33.95	31.96	35.59	30.36	22.39
					Synergy					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
41				1	2.93	3.32	10.08			
42				2	4.10	6.76	1.43			
43				3	0.96	4.59	7.04			
44				4	1.43	3.59	9.57			
Component performances										
					Measured					
					FSC	CRC	AUL			
					g/g	g/g	g/g			
Starch type 1: Pregel 2604 (ADM)					6.50	4.70	11.47			
Starch type 2: Carboxymethyl crosslinked with TEG					28.00	19.00	30.70			
Starch type 3: Maleate crosslinked with TEG					20.00	10.00	28.81			
Starch type 4: Hybrid crosslinked with TEG					20.00	12.00	23.14			
Guar gum (Starlight)					48.73	45.68	22.60			
Konjac gum (LIMAO)					46.73	43.89	19.62			

**EXAMPLES 45 to 50****Effect on the FSC, CRC and AUL of multi-component blends, of  
different polysaccharides**

- Blends were prepared by mixing pregelatinized wheat starch
- 5 (ADM), as the first component class (starch based product), guar gum (Starlight) and konjac gum (LIMAO) as the second component class (polygalactomanan and polyglucomanan) and finally, CMC (Hercules), xanthan (ADM), sodium alginate (Tic Gums), carrageenan (CP Kelco), pectine (Tic Gums) and chitosan (Primex) as the third component class (ionic class) as
- 10 described in Example 1 to 15. The synergistic results on the FSC, CRC and AUL are illustrated in Table VII.

TABLE VII: Examples for multi-component blends											
Ex.	Blends								Measured		
	Starch	Guar	Konjac	CMC	Xanthan	Alginate	Carrageenan	Pectine	FSC	CRC	AUL
	%	%	%	%	%	%	%	%	g/g	g/g	g/g
45	40.00	30.00	0.00	20.00	0.00	10.00	0.00	0.00	32.89	29.38	23.41
46	30.00	37.50	0.00	22.50	0.00	10.00	0.00	0.00	38.13	34.00	23.48
47	30.00	20.00	20.00	10.00	10.00	0.00	10.00	0.00	41.30	38.83	20.76
48	30.00	20.00	20.00	10.00	10.00	0.00	0.00	10.00	38.86	35.30	19.00
49	30.00	20.00	20.00	10.00	0.00	0.00	10.00	10.00	42.39	38.88	21.73
50	30.00	20.00	20.00	10.00	0.00	10.00	0.0	10.00	36.51	32.28	25.10
	Calculated				Synergy						
	FSC	CRC	AUL		FSC	CRC	AUL				
	g/g	g/g	g/g		g/g	g/g	g/g				
	45	32.38	25.42		19.52	0.51	3.96		3.89		
46	36.69	29.30	20.76	1.44	4.70	2.72					
47	38.99	33.11	19.66	2.31	5.72	1.10					
48	38.59	32.73	18.54	0.27	2.57	0.46					
49	34.85	29.42	18.73	7.54	9.46	2.99					
50	35.11	28.47	18.79	1.40	3.81	6.31					
Component performances											
				Measured							
				FSC	CRC	AUL					
				g/g	g/g	g/g					
Starch 2604 (ADM)				6.50	4.70	11.47					
Guar gum (Starlight)				48.73	45.68	22.60					
Konjac gum (LIMAO)				46.73	43.89	19.62					
CMC (Aqualon B315)				58.20	45.90	27.41					
Sodium Alginate (Tic Gums)				47.63	24.35	26.73					
Carrageenan (CP Kelco)				45.02	33.88	26.14					
Pectine (Tic Gums)				41.02	30.06	14.95					
Xanthan (ADM)				82.46	67.02	24.20					
Chitosan (Primex)				8.18	1.63	16.14					

**EXAMPLES 51 to 57****Effect on the FSC, CRC and AUL of multi-component blends, of  
different polysaccharides with the presence of proteins**

Blends were prepared by mixing gelling proteins such as  
5 gelatin and calcium caseinate with pregelatinized wheat starch (ADM), as the  
first component class (modified starch), guar gum (Starlight) and konjac gum  
(LIMAO) as the second components class (polygalactomanan and  
polyglucomanan) and finally, CMC (Hercules), xanthan (ADM), sodium  
alginate (Tic Gums), carrageenan (CP Kelco), pectine (Tic Gums) and  
10 chitosan (Primex) as the third components class (ionic class) as described in  
Examples 1 to 15. The synergistic results on the FSC, CRC and AUL are  
illustrated in Table VIII.

TABLE VIII: Examples for multi-component blends with proteins											
Ex.	Blends										
	Starch	Guar	Konjac	CMC	Xanthan	Alginate	Carra- geenan	Pectine	Chitosan	Gelatin	Casein
	%	%	%	%	%	%	%	%	%	%	%
51	50.00	0.00	0.00	0.00	0.00	14.50	14.50	14.50	1.50	0.00	5.00
52	50.00	16.00	0.00	0.00	0.00	14.50	14.50	0.00	0.00	0.00	5.00
53	50.00	16.00	0.00	0.00	0.00	14.50	14.50	0.00	0.00	5.00	0.00
54	35.00	50.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	15.00	0.00
55	55.00	10.00	17.00	5.00	2.00	0.00	5.00	0.00	0.00	5.00	1.00
56	45.00	26.00	5.00	5.00	5.00	2.00	2.00	2.00	0.00	6.00	2.00
57	35.00	50.00	0.00	0.00	0.00	5.00	0.00	0.00	0.00	5.00	5.00
	Measured				Calculated				Synergy		
	FSC	CRC	AUL		FSC	CRC	AUL		FSC	CRC	AUL
	g/g	g/g	g/g		g/g	g/g	g/g		g/g	g/g	g/g
51	28.38	19.75	17.35		23.00	15.18	16.58		5.38	4.57	0.77
52	32.53	25.09	21.21		24.73	18.10	17.78		7.80	6.99	3.43
53	30.08	23.91	19.81		25.11	18.41	17.86		4.97	5.50	1.95
54	31.23	28.78	22.35		28.52	25.41	17.83		2.71	3.37	4.52
55	29.59	26.84	19.71		23.88	20.25	16.06		5.71	6.59	3.65
56	31.98	27.76	19.27		28.49	23.97	17.27		3.49	3.79	2.00
57	32.21	29.09	19.90		29.89	26.01	18.26		2.32	3.08	1.64
Component performances											
					Measured						
					FSC	CRC	AUL				
					g/g	g/g	g/g				
	Starch 2604 (ADM)				6.50	4.70	11.47				
	Guar gum (Starlight)				48.73	45.68	22.60				
	Konjac gum (LIMAO)				46.73	43.89	19.62				
	CMC (Aqualon B315)				58.20	45.90	27.41				
	Sodium Alginate (Tic Gums)				47.63	24.35	26.73				
	Carrageenan (CP Kelco)				45.02	33.88	26.14				
	Pectine (Tic Gums)				41.02	30.06	14.95				
	Xanthan (ADM)				82.46	67.02	24.20				
	Chitosan (Primex)				8.18	1.63	16.14				
	Gelatin				12.56	6.15	16.80				
	Casein				4.90	0.00	15.35				

Although the present invention has been described hereinabove by way of preferred embodiments thereof, it can be modified

5 without departing from the spirit and nature of the subject invention as defined in the appended claims.



## **REFERENCES**

1. Beenackers A. A. C. M. et al. An experimental study on the carboxymethylation of granular potato starch in non-aqueous media. Carbohydr. Polym., 2001, 45, 219-226.
- 5                   2. EDANA, Absorbency Against Pressure No. 442.1-99, Recommended Test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Absorbency Against Pressure by Gravimetric Determination, Febr. 1999.
- 10               3. EDANA, Free Swell Capacity No. 440.1-99, Recommended test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Free Swell Capacity in Saline by Gravimetric Determination, Febr. 1999.
- 15               4. EDANA, Centrifuge Retention Capacity No. 441.1-99, Recommended Test Method: Superabsorbent materials-Polyacrylate superabsorbent powders-Centrifuge Retention Capacity in Saline by Gravimetric Determination, Febr. 1999.
5. US Environmental Protection Agency (EPA), Fate, Transport and Transformation Test Guidelines, OPPTS 832.3200, Zahn-Wellens / EMPA test, EPA712-C-98-084, January 1998.
- 20               6. ASTM D6355-98 Standard Test Method for Human Repeat INSULT Patch Testing of Medical Gloves.

**WHAT IS CLAIMED IS:**

1. A multi-component synergistic absorbent composition comprising one or more modified starches and at least one or more components selected from a first component class selected from  
5 mannose containing polysaccharides, a second component class selected from ionic polysaccharides, and a third component class selected from gelling proteins or polypeptides.
2. A multi-component synergistic absorbent composition as defined in claim 1, wherein said first component class is  
10 selected from the group consisting of guar gum, locust bean gum, tara gum, konjac gum or konjac flour, fenugreek gum, mesquite gum and aloe mannans.
3. A multi-component synergistic absorbent composition as defined in claim 1, wherein said first component class is  
15 selected from the group consisting of locust bean gum, tara gum, konjac gum or konjac flour, fenugreek gum, mesquite gum and aloe mannans.
4. A multi-component synergistic absorbent composition as defined in claim 1, wherein said second component class is  
20 selected from the group consisting of carboxyalkylated cellulose, carboxymethyl cellulose, oxidized cellulose, sulfated cellulose, cationic cellulose, pectin, chitosan salts, arabic gum, karaya gum, kappa, iota and  
lambda carrageenan gums, agar-agar and alginates.
5. A multi-component synergistic absorbent composition as defined in claim 1, wherein said second component class is  
25 selected from the group consisting of carboxyalkylated cellulose, carboxymethyl cellulose, oxidized cellulose, sulfated cellulose, cationic cellulose, pectin, chitosan salts, xanthan gum, arabic gum, karaya gum, kappa, iota and lambda carrageenan gums, agar-agar and alginates.

6. A multi-component synergistic absorbent composition as defined in claim 1, wherein said third component class is selected from the group consisting of gelatin, albumin, collagen, keratin, keratose, fibrin, ovalbumin, bovine albumin, polyaspartic acid and its salts, casein and its salt, Whey proteins, Whey protein isolates, soybean proteins, soy proteins, soy proteins isolates, zein and gluten.

7. A multi-component synergistic absorbent composition as defined in claims 1 to 6, exhibiting synergistic effects on absorption under load, centrifuge retention or free swell capacity.

8. A multi-component synergistic absorbent composition comprising one or more ionic polysaccharides and at least one or more components selected from a first component class selected from mannose containing polysaccharides and a second component class selected from gelling proteins or polypeptides.

9. A multi-component synergistic absorbent composition as defined in claim 8, wherein said ionic polysaccharides are selected from the group consisting of carboxyalkylated cellulose, carboxymethyl cellulose, oxidized cellulose, sulfated cellulose, cationic cellulose, pectin, chitosan salts, arabic gum, karaya gum, kappa, iota and lambda carrageenans, agar-agar and alginates.

10. A multi-component synergistic absorbent composition as defined in claim 8, wherein said ionic polysaccharides are selected from the group consisting of carboxyalkylated cellulose, carboxymethyl cellulose, oxidized cellulose, sulfated cellulose, cationic cellulose, pectin, chitosan salts, xanthan gum, arabic gum, karaya gum, kappa, iota or lambda carrageenans, agar-agar and alginates.

11. A multi-component synergistic absorbent composition as defined in claim 8, wherein said first component class is

selected from the group consisting of guar gum, locust bean gum, tara gum, konjac gum or konjac flour, fenugreek gum, mesquite gum and aloe mannans.

12. A multi-component synergistic absorbent composition as defined in claim 8, wherein said first component class is  
5 selected from the group consisting of locust bean gum, tara gum, konjac gum, konjac flour, fenugreek gum, mesquite gum and aloe mannans.

13. A multi-component synergistic absorbent composition as defined in claim 8, wherein said second component class is  
10 selected from the group consisting of gelatin, albumin, collagen, keratin, keratose, fibrin, ovalbumin, bovine albumin, polyaspartic acid and its salts, casein and its salt, Whey proteins, Whey protein isolates, soybean proteins, soy proteins, soy proteins isolates, zein and gluten.

14. A multi-component synergistic absorbent composition as defined in claims 8 to 13, exhibiting synergistic effects on  
15 absorption under load, centrifuge retention or free swell capacity.

15. A multi-component synergistic absorbent composition as defined in claim 1, wherein said modified starches are obtained  
20 from the group consisting of corn, waxy corn, wheat, waxy wheat, rice, waxy rice, potato, tapioca, waxy maize, high amylose content corn starch, sorghum, waxy sorghum, sago, barley, amaranth, and mixture thereof.

16. A multi-component synergistic absorbent composition as defined in claim 15, wherein said modified starches are  
25 obtained by procedures selected from the group consisting of pregelatinization, thermal inhibition, extrusion, jet-cooking, dextrination, hydrolysis, oxidation, covalent cross-linked, alkylation, hydroxyalkylation, carboxyalkylation, esterification, fractionating in its amylose or amylopectin content, and combinations thereof.

17. A multi-component synergistic absorbent composition as defined in claims 4, 5, 9 and 10, wherein said ionic polysaccharides are cationic polysaccharides.

5 18. A multi-component synergistic absorbent composition as defined in claim 17, wherein said cationic polysaccharides are selected from the group of salts consisting of chlorides, bromides, iodides, nitrates, phosphates, sulfates and organic salts.

10 19. A multi-component synergistic absorbent composition as defined in claims 4, 5, 9 and 10, wherein said ionic polysaccharides are anionic polysaccharides.

20. A multi-component synergistic absorbent composition as defined in claim 19, wherein said anionic polysaccharides are selected from the group of salts consisting of sodium, lithium, potassium, and ammonium.

15 21. A multi-component synergistic absorbent composition as defined in claims 2, 3, 11 and 12, wherein said mannose containing polysaccharides are modified by procedures selected from the group consisting of hydrolysis, oxidation, covalent cross-linking, alkylation, hydroxyalkylation, carboxyalkylation and esterification.

20 22. A multi-component synergistic absorbent composition as defined in claims 4, 5, 9 and 10, wherein said ionic polysaccharides are modified by procedures selected from the group consisting of hydrolysis, oxidation, covalent cross-linking, alkylation, hydroxyalkylation, carboxyalkylation and esterification.

25 23. A multi-component synergistic absorbent composition as defined in claims 6 and 13 wherein said gelling proteins or polypeptides are modified by procedures selected from the group consisting

of hydrolysis, oxidation, covalent cross-linking, alkylation, hydroxyalkylation, carboxyalkylation and esterification.

24. A multi-component synergistic absorbent composition as defined in claims 21, 22 and 23, comprising at least two  
5 modified gelling and renewable polymers selected from modified mannose containing polysaccharides, modified ionic polysaccharides and modified gelling proteins or polypeptides.

25. A multi-component synergistic absorbent composition as defined in claim 1, wherein said modified starches and said  
10 first, second and third component class have a mean particle size ranging from about 80  $\mu\text{m}$  to about 800  $\mu\text{m}$ .

26. A multi-component synergistic absorbent composition as defined in claim 25, wherein said modified starches and said  
15 first, second and third component class have a mean particle size ranging from about 150  $\mu\text{m}$  to about 600  $\mu\text{m}$ .

27. A multi-component synergistic absorbent composition as defined in claim 26, wherein the particle size of said modified starches and of said first, second and third component class differs by no more than 200  $\mu\text{m}$ .

28. A multi-component synergistic absorbent composition as defined in claim 8, wherein said ionic polysaccharides and said  
20 first, second and third component class have a mean particle size ranging from about 80  $\mu\text{m}$  to about 800  $\mu\text{m}$ .

29. A multi-component synergistic absorbent composition as defined in claim 28, wherein said ionic polysaccharides and  
25 said first, second and third component class have a mean particle size ranging from about 150  $\mu\text{m}$  to about 600  $\mu\text{m}$ .

30. A multi-component synergistic absorbent composition as defined in claim 29, wherein the particle size of said ionic polysaccharides and of said first, second and third component class differs by no more than 200  $\mu\text{m}$ .

5                   31. A blood or menses absorbent member comprising an absorbent composition as defined in claims 1 to 30, and cellulosic fibers, synthetic fibers or a mixture thereof.

                  32. A sanitary napkin comprising an absorbent composition as described in claims 1 to 30, or an absorbent member as  
10 defined in claim 31, or a combination thereof.

                  33. A medical device comprising an absorbent composition as described in claims 1 to 30, or an absorbent member as defined in claim 31, or a combination thereof.

                  34. A urine, physiological fluid or liquid feces absorbent  
15 member comprising an absorbent composition as defined in claims 1 to 30, and cellulosic fibers, synthetic fibers or a mixture thereof.

                  35. A diaper comprising an absorbent composition as described in claims 1 to 30, an absorbent member as defined in claim 31, or a combination thereof.

20                   36. An incontinence garment comprising an absorbent composition as described in claims 1 to 30, an absorbent member as defined in claim 31, or a combination thereof.

                  37. A food fluid absorbent member comprising an absorbent composition as described in claims 1 to 30, and cellulosic fibers,  
25 synthetic fibers or a mixture thereof.

38. A food pad containing an absorbent composition as described in claims 1 to 30, an absorbent member defined in claim 31, or a combination thereof.

5 39. An artificial snow agent, comprising an absorbent composition as defined in claims 1 to 30.

40. A drug delivery agent comprising an absorbent composition as defined in claims 1 to 30.

41. A cosmetic agent comprising an absorbent composition as defined in claims 1 to 30.

10 42. A cat litter absorbent comprising an absorbent composition as defined in claims 1 to 30.

43. A soil humidity retaining agent comprising an absorbent composition as defined in claims 1 to 30.

15 44. A fire retarding agent comprising an absorbent composition as defined in claims 1 to 30.

45. A process for producing the multi-component synergistic absorbent compositions of claim 1, comprising blending the modified starches with at least one or more components of said first, second and third component class.

20 46. A process for producing the multi-component synergistic absorbent compositions of claim 8, comprising blending the ionic polysaccharides with at least one or more components of said first and second component class.

25 47. A process as defined in claims 45 and 46 wherein said blending is dry-blending.



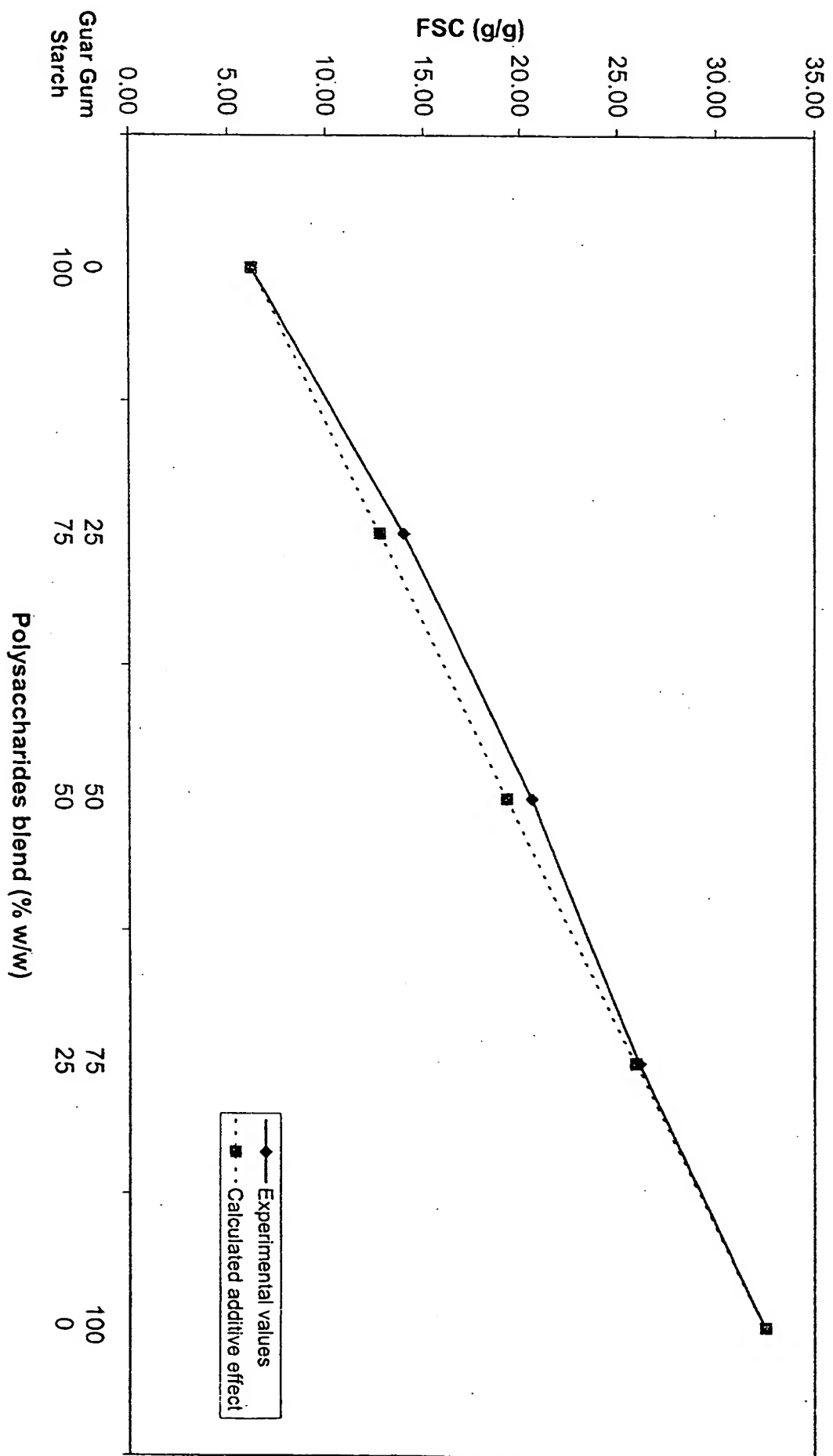


Figure 1.

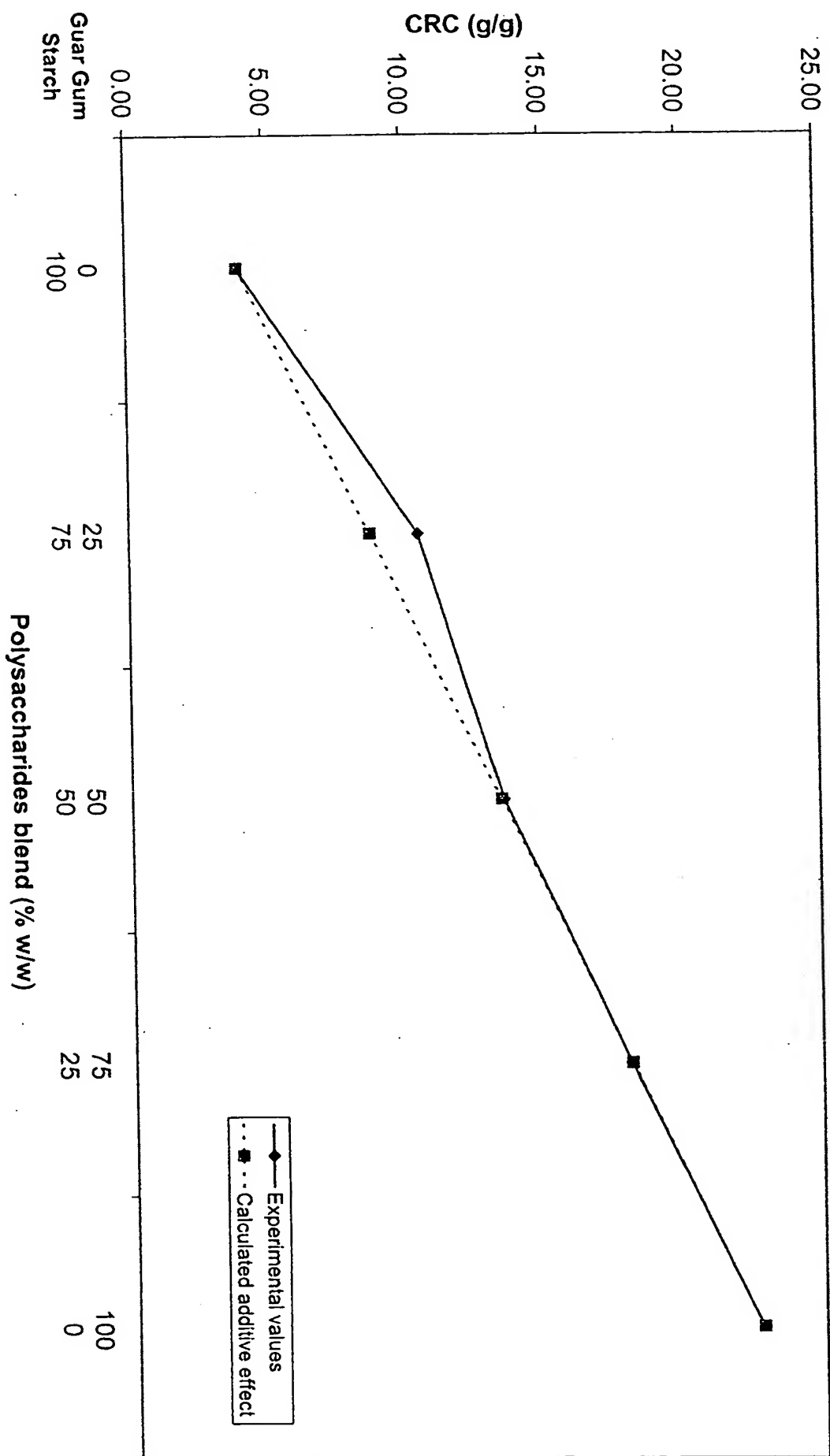


Figure 2.

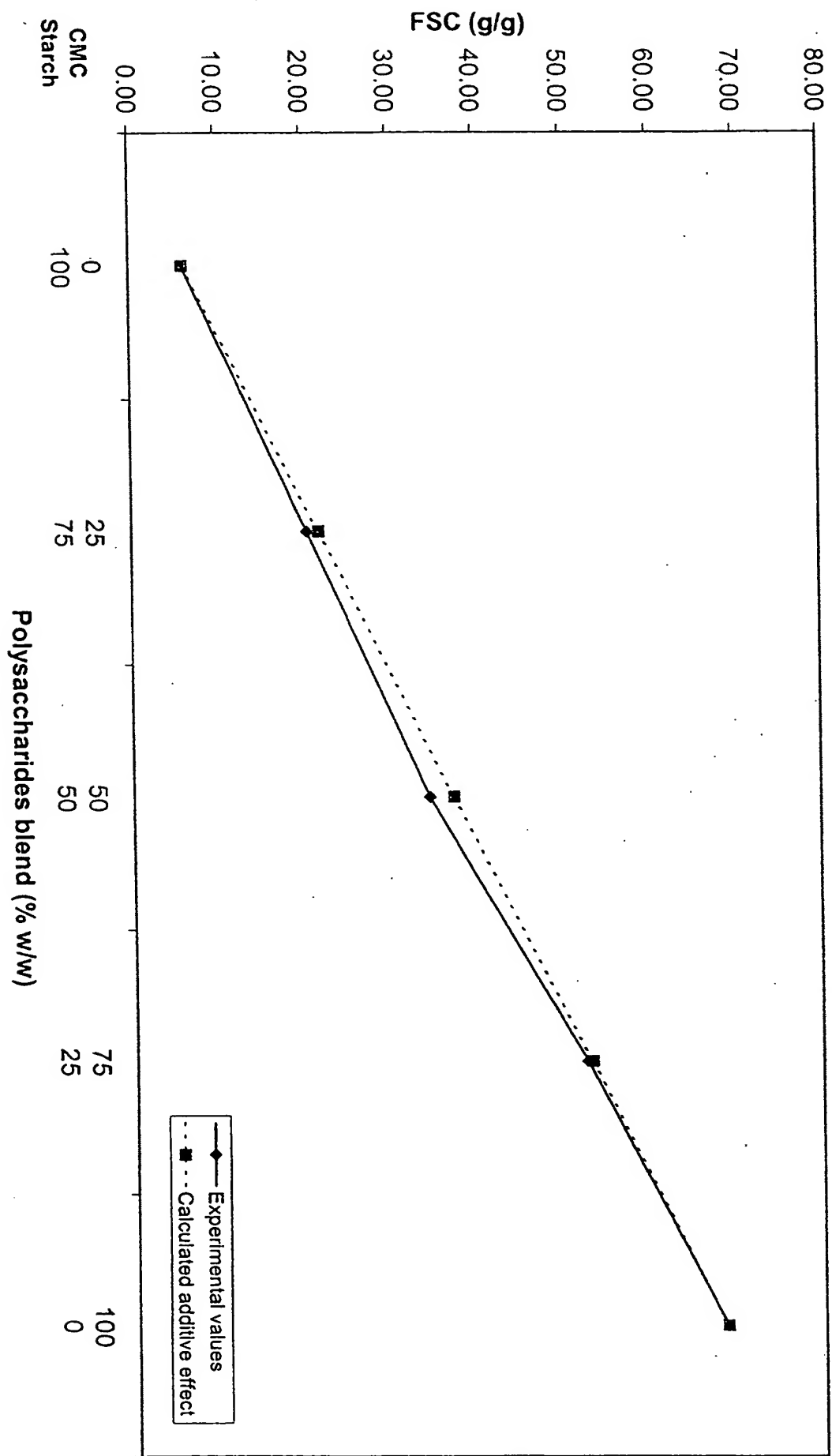


Figure 3.

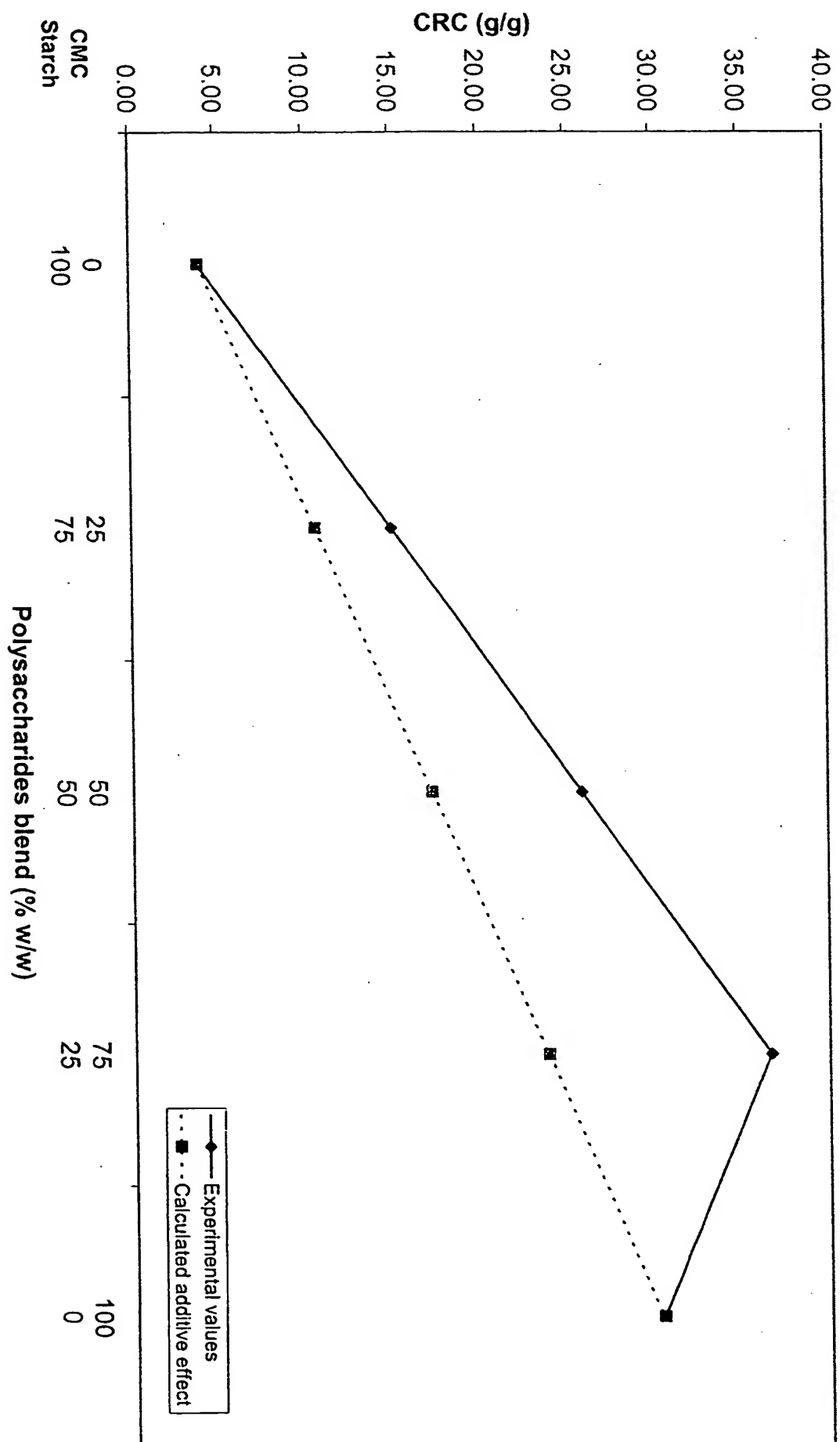


Figure 4.

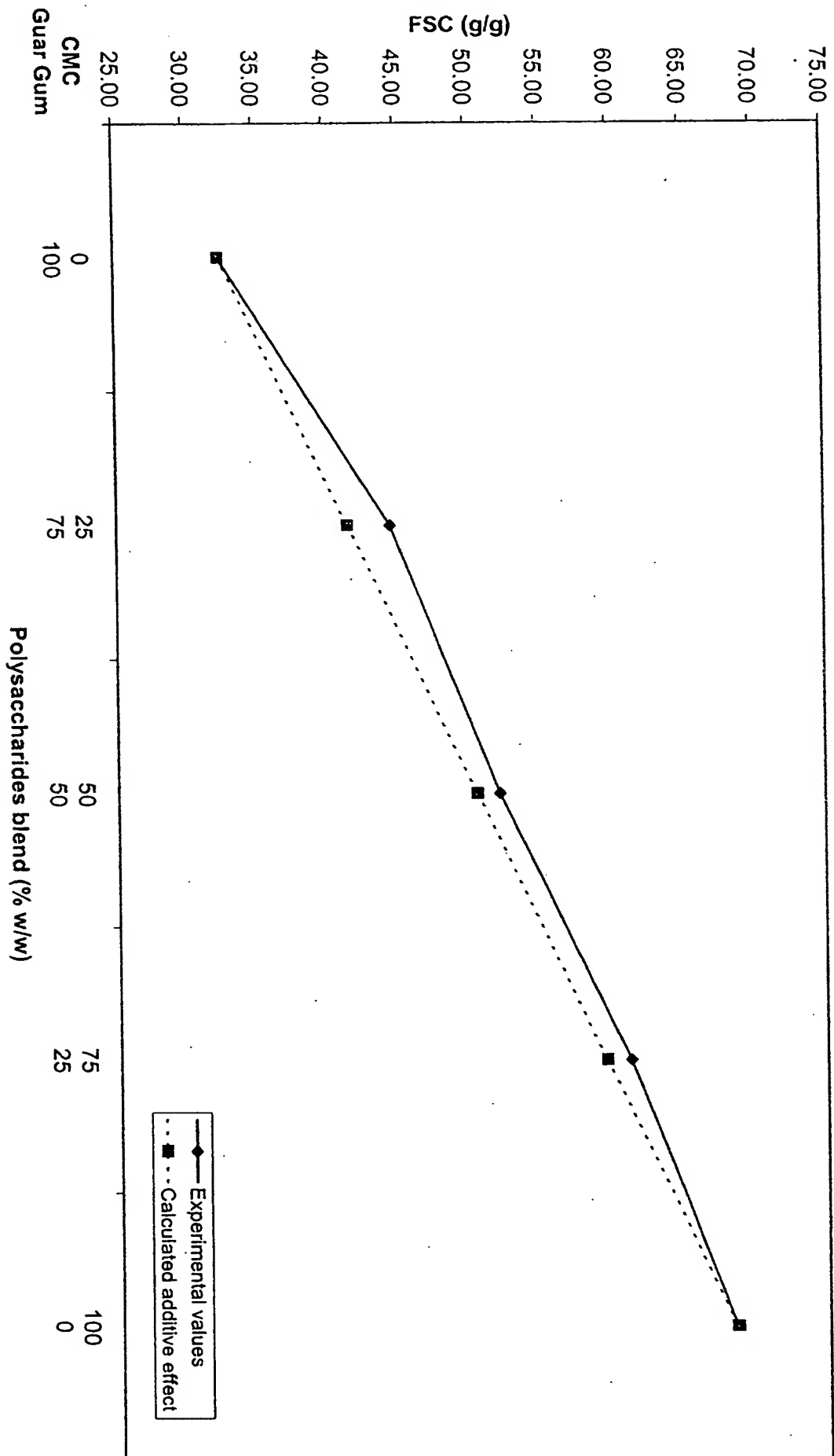


Figure 5.

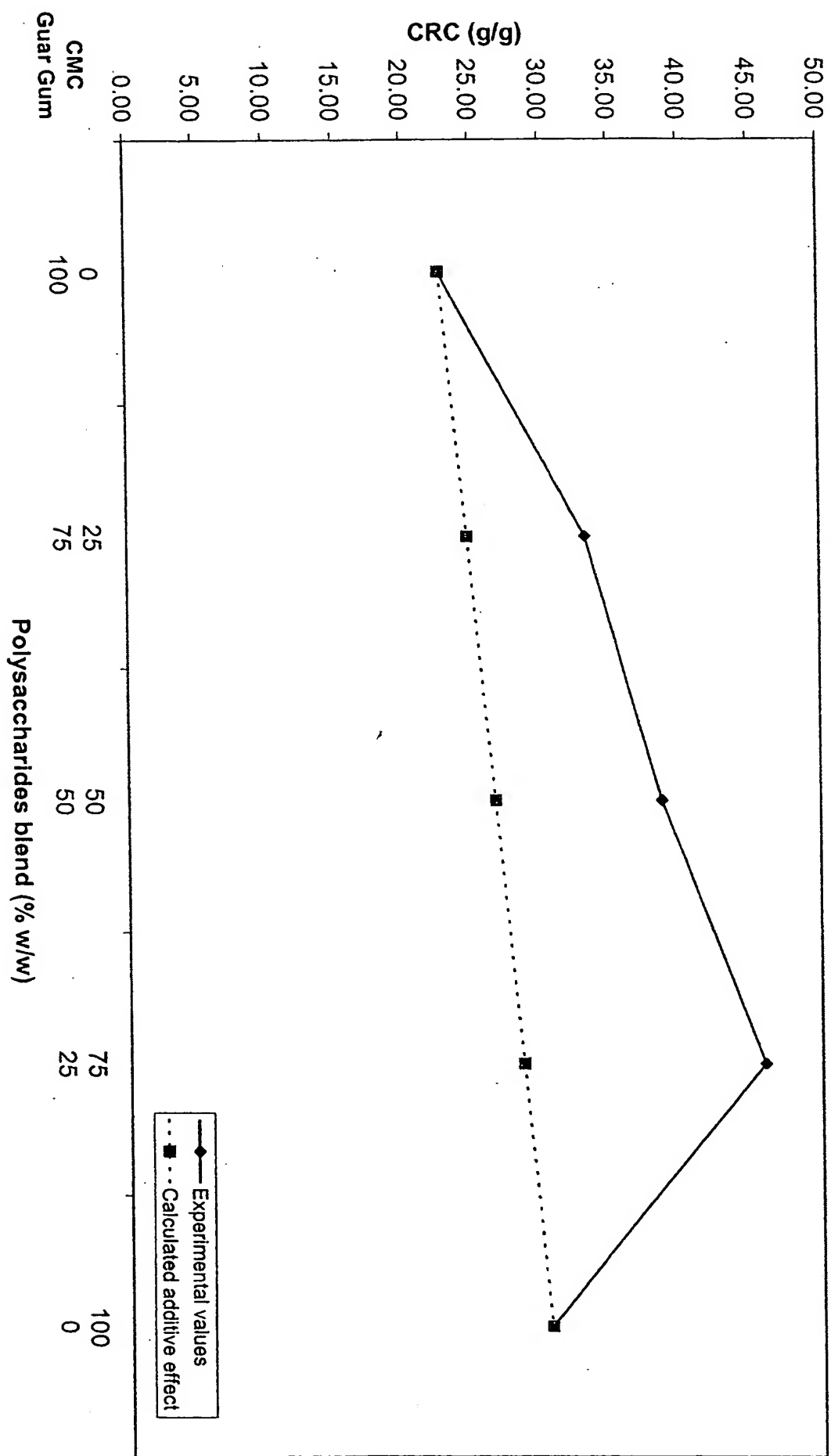


Figure 6.

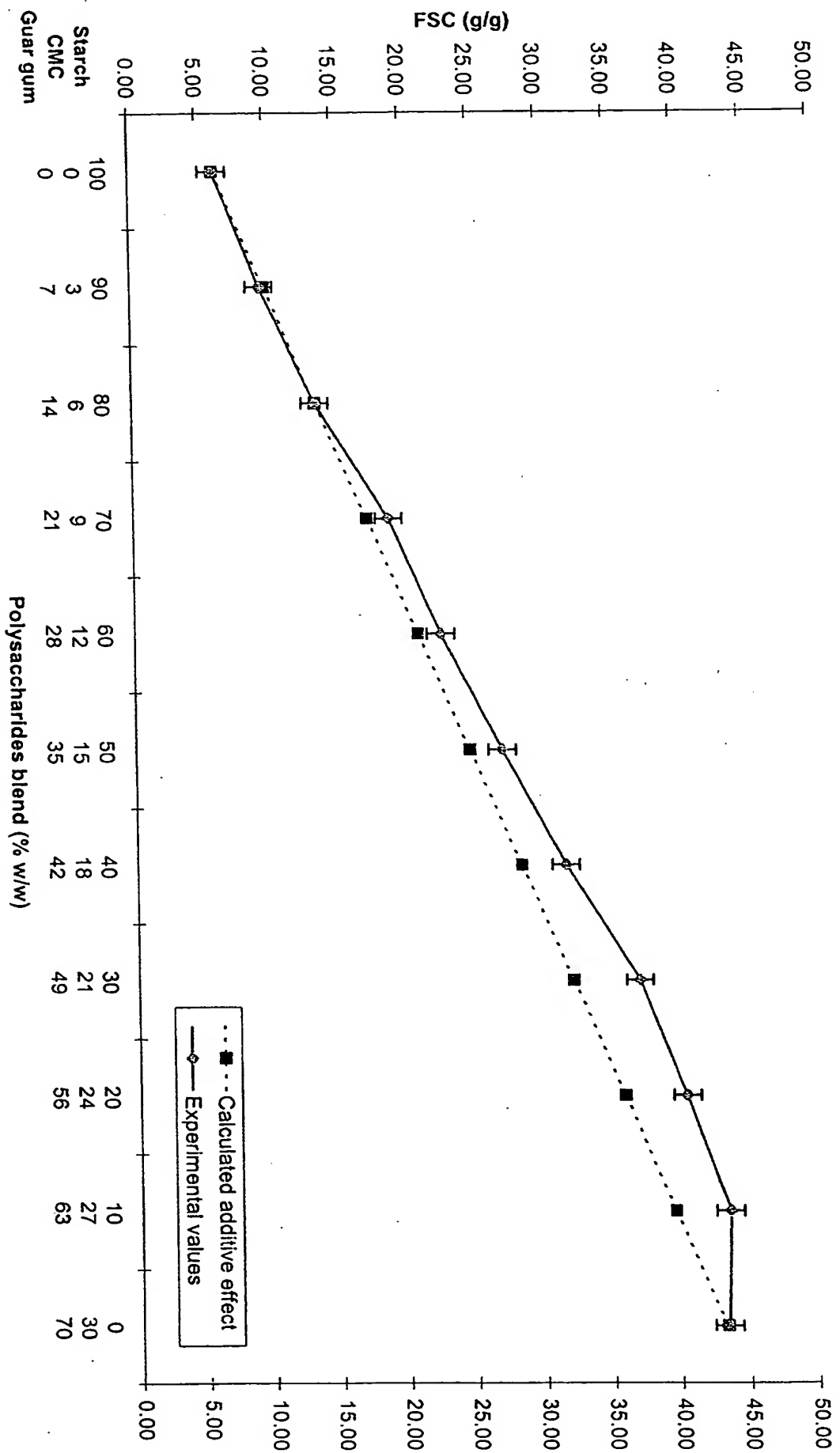


Figure 7.

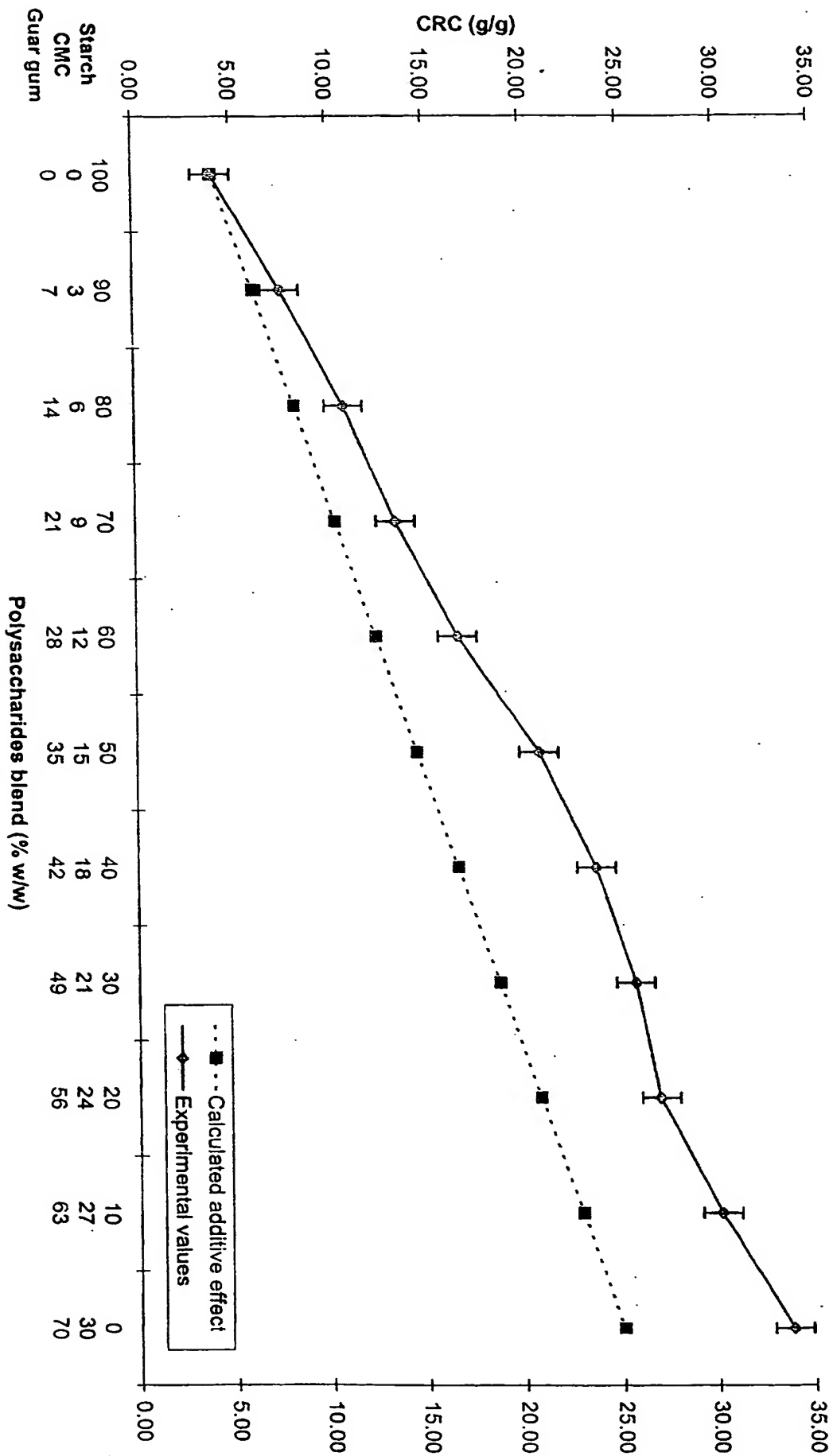


Figure 8.



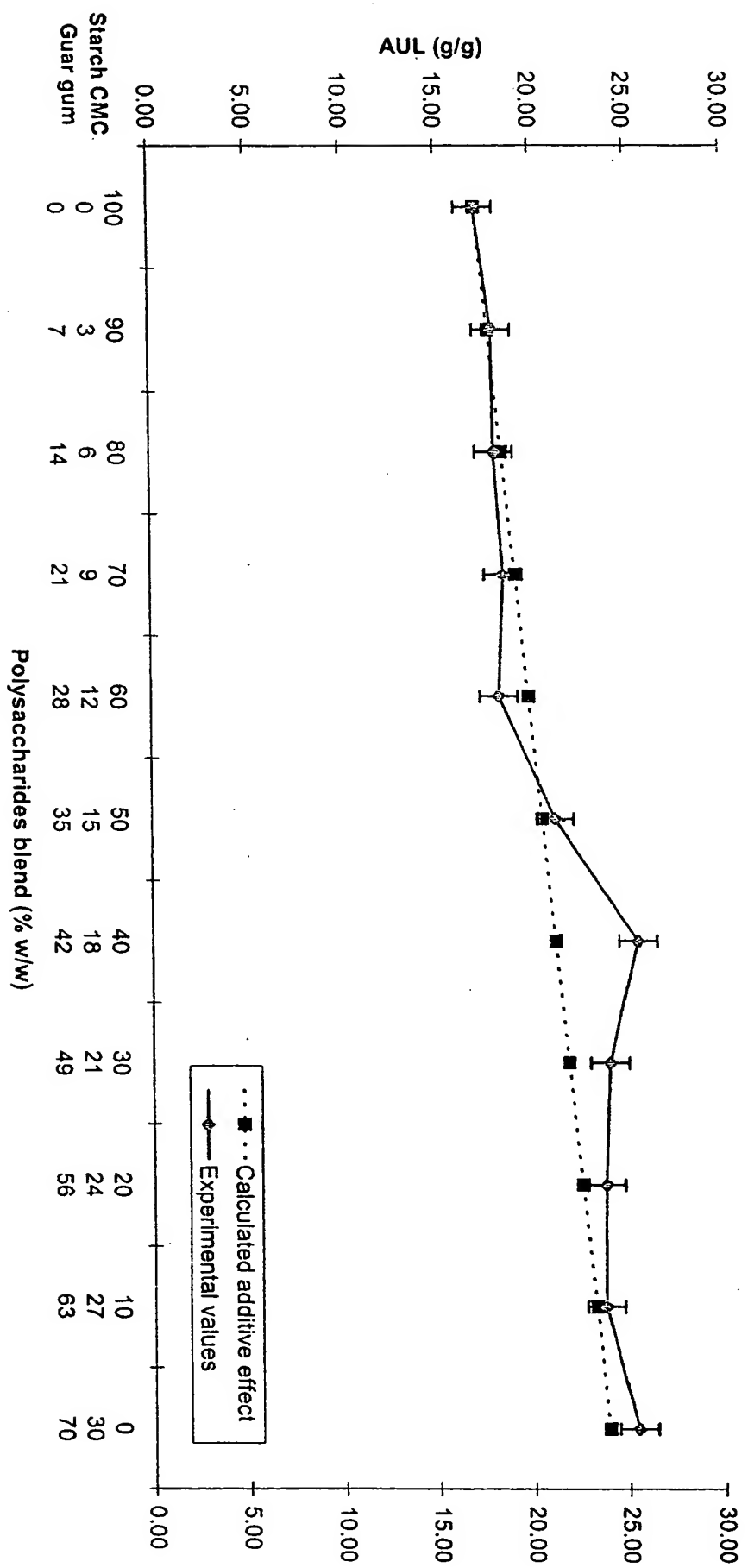


Figure 9.

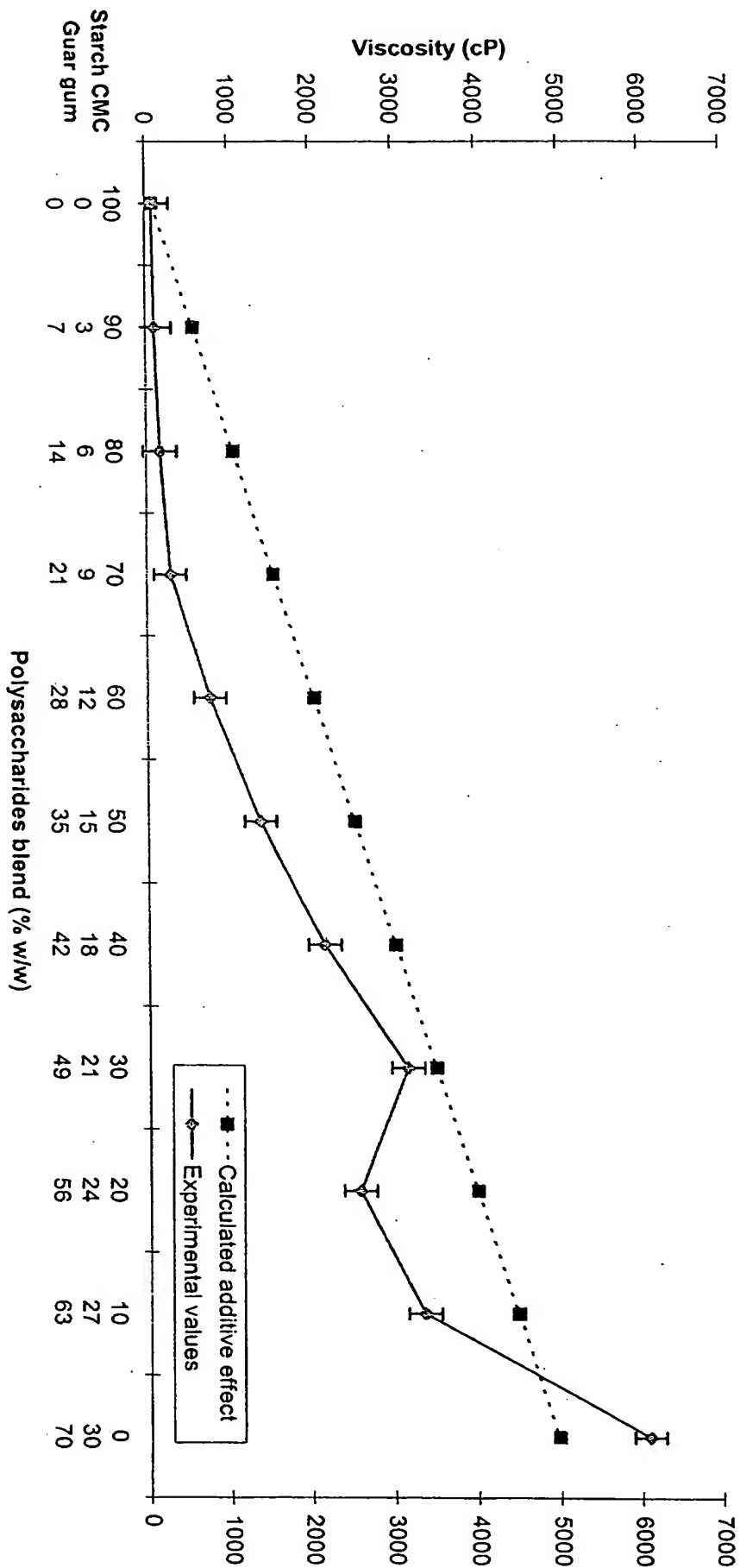


Figure 10.

### **ABSTRACT OF THE DISCLOSURE**

The present invention relates to multi-component synergistic absorbent compositions comprising at least one polysaccharide and at least one or more polysaccharide-based components or gelling proteins. These  
5 compositions possess synergistic effects in their capacity to absorb water, saline solutions and biological fluids, at normal pressure or under load, or to retain these fluids, or a combination of these properties.